Composition and Reaction Modeling of Hydroconversion of Lignins

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Highlights

- Composition modeling allows to reconstruct molecular-level information on lignin structures.
- Good agreement was obtained between lignin analyses and surrogate lignin mixture properties.
- Molecular-level reaction modeling was performed using Gillespie's Stochastic Simulation Algorithm.
- Prediction of conversion and overall yield structure in good agreement with experimental data.

1. Introduction

To convert lignocellulosic biomass into liquids (bio-oils), a large spectrum of thermochemical processes, such as pyrolysis, hydroconversion and catalytic cracking, are currently being developed. However, the high structural complexity of lignocellulosic materials hampers its accurate analytical characterization, as well as the understanding of the conversion mechanisms and their kinetics. In this work, a stochastic methodology has been developed to model the conversion of lignin. Starting from a probabilistic representation of lignin, a kinetic Monte Carlo (kMC) approach was applied to biomass conversion.

2. Methods

A representation of the lignin structure on the molecular level cannot be directly obtained from the available analyses, owing to its structural complexity. Hence, these samples are generally characterized by several different analytical techniques, which all highlight different characteristics of the sample. In a first step, the available analytical information for the lignin is transformed into a set of molecules that has the same average properties. To represent lignins, Klein and Virk [1] used a 6x8 matrix of probabilities of occurrence for different types of aromatic units in the structure. Each row of the matrix is a specific type of methoxyphenol and each column a type of 3-carbon-atom side chain or inter-unit linkage. Each matrix element a_{jk} represents the probability of occurrence of an aromatic unit composed by a ring equal to the type j of methoxyphenol and a lateral chain of the type k. During lignin conversion, however, other structures start to appear. In our work, this representation for the initial lignin has therefore been extended to a 44x22 matrix by including additional lignin moieties and additional linkages to account for the various structures formed during lignin conversion. From this probability matrix, a representative set of molecules is created by sampling the matrix.

After the composition modeling step, the generated set of molecules is used as input for the molecule-based kinetic modeling of the hydroconversion of lignin. From this representation of the initial lignin and a list of possible reactions, the transformation of the lignin was simulated by means of a kMC algorithm proposed by Gillespie [2] and termed Stochastic Simulation Algorithm (SSA). Details of the algorithm can be found elsewhere [3]. This method describes the reaction system at the molecular level by following the transformations of a discrete population of molecules. The corresponding reaction parameters are determined from literature based on model compounds with a similar structure to that of the elements in the matrix.

3. Results and discussion

The above-described method was applied to a wheat straw soda lignin (Protobind 1000). The Protobind 1000 lignin was characterized by elemental analysis, ^{1}H-NMR, ^{13}C-NMR, and Gel Permeation

Chromatography. After phosphitylation, a ^{31}P-NMR analysis was also performed. Detailed information on these techniques and their results can be found elsewhere [3]. This lignin had an average molecular weight of 4915 g/mol. Its elemental analysis showed that the lignin contained 65 wt% of carbon, 28 wt% of oxygen, 6 wt% of hydrogen and 1 wt% of nitrogen.

From these analytical data, a matrix of occurrence probabilities was created. After resampling, the set of molecules closely represents the Protobind 1000, as illustrated in Figure 1 for the ^{13}C-NMR analysis. For the elemental analysis, the molecular weight and polydispersion index, a similar agreement was obtained.

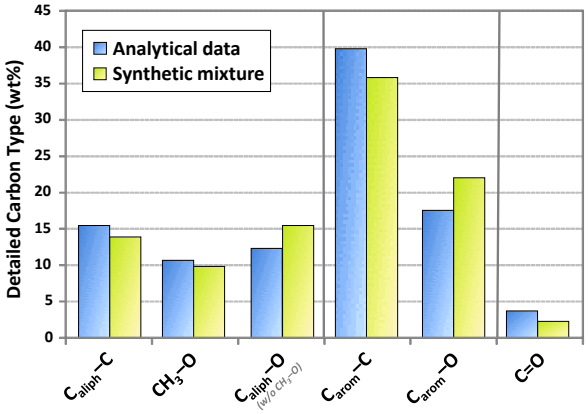

Figure 1. Composition modeling: ^{13}C NMR families of the native lignin

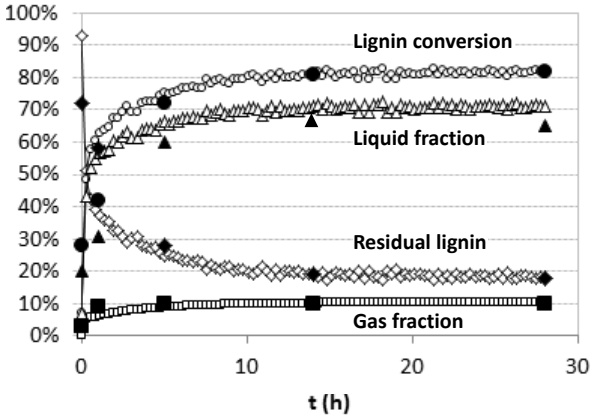

Figure 2. Reaction modeling: Evolution of the lignin conversion and the product fractions: experimental (black) vs. simulated (white)

The kMC algorithm was used to simulate the conversion of the lignin, and accurately predicts the yields of gas, liquid and solid (Figure 2), the gas composition, the composition of the bio-oil (elemental analysis, functional groups), and the molecular weight and polydispersion index of the residual lignin.

4. Conclusions

A probabilistic representation of Protobind 1000 lignin was created based on a matrix that reflects the occurrence probability of a set of structural elements. The initial lignin was represented by a matrix of 16 aromatic rings and 6 inter-unit linkages, whose combination leads to 96 substructures. By sampling this matrix, a representative set of molecules was created and used as input for the kinetic modeling. The number of available substructures was increased to 968 by extending the matrix with chemical moieties produced during the conversion of lignin. The hydroconversion of lignin was then simulated by means of a molecule-based kinetic Monte Carlo method.

This methodology was shown to be a valid tool for the representation of lignin polymers, providing a set of realistic structures of this complex co-polymer whose average properties accurately fit to the information from experimental analyses. A good agreement was obtained between simulated and experimental data for both the composition and the characteristics of the initial lignin. The kinetic Monte Carlo reaction model also correctly predicts the various effluents resulting from the lignin hydroconversion. This simulation technique has the advantage that it does not require a pre-defined kinetic network since it is generated “on-the-fly” as the reactions proceed.

References

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Keywords
Lignin ; Composition modeling ; Molecular reconstruction ; Stochastic Simulation Algorithm.